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⑥⑤ Chelate resins, process for their production and their use.

⑥⑦ Described are chelate resins having a functional group of the formula:  $\text{—C} = \text{NOH}$ , wherein  $R_1$  and  $R_2$  are each



independently hydrogen, alkyl, aminoalkyl, phenyl or a substituted group thereof and another functional group of the formula:  $\text{—C} = \text{NH}$ , wherein  $R_3$  is amino, alkylamino,



polyethylenepolyamino, hydrazo, hydrazino, hydrazono, amidino, guanidino, semicarbazide or a substituted group thereof. These resins have an excellent adsorption capacity for metal ions.

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CHELATE RESINS, PROCESS FOR THEIR PRODUCTION  
AND THEIR USE

This invention relates to chelate resins and a process for producing the same and their use for removing metal ions from liquids containing metal ions.

Chelate resins are very useful for the purification of industrial water, the treatment of waste water, the recovery of valuable metal elements, and the like because when they are used, metal ions can selectively be removed from a liquid containing the metal ions.

It has heretofore been well known that a resin having amidoxime groups is produced by reacting a resin having nitrile groups with hydroxylamine and/or a derivative thereof, and that the thus obtained resin satisfactorily adsorbs metal ions such as uranium, gold, iron, mercury, copper, lead and the like (U.S. Patent No. 3,088,799, Published Unexamined Japanese Patent Application Nos. 53,593/76, and 126,088/78). However, said chelate resin has small adsorption capacity and is desired to be improved in this point.

Recently, in order to improve such a disadvantage of said chelate resin, there has been proposed a process for producing a chelate resin having amidoxime groups by subjecting to polymerization a monomer mixture comprising a crosslinking agent selected from the group consisting of polyacrylates of polyalkylene polyols whose alkylene groups have 2 to 4 carbon atoms, and polymethacrylates of said polyols, and an ethylenically

1 unsaturated compound having one or more nitrile groups,  
and then reacting the resulting polymer with hydroxyl-  
amine (Published Unexamined Japanese Patent Application  
No. 53,106/81). The improved chelate resin described  
5 above has an improved metal ion adsorption rate as compared  
with conventional resins having amidoxime groups but does  
not always have a sufficiently improved adsorption  
capacity for metal ions. Therefore, when a large amount  
of a liquid is subjected to adsorption treatment, the im-  
10 proved chelate resin is disadvantageous, for example, in  
that the amount treated per unit time decreases, that  
many treating apparatuses are needed, and that the  
construction and operation costs increase.

In consideration of these circumstances, in  
15 order to produce an amidoxime group type chelate resin  
having an excellent adsorption capacity and a high adsorp-  
tion rate as compared with well-known amidoxime group  
type chelate resins, the present inventors have  
devoted themselves to investigations to accomplish  
20 this invention.

This invention provides a chelate resin having  
a functional group represented by the formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are each independently a hydrogen atom,

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- 1 an alkyl group, an aminoalkyl group, a phenyl group or substituted group thereof, and a functional group represented by the formula:



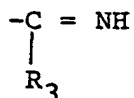
- wherein  $\text{R}_3$  is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group, or a substituted group thereof.

- This invention further provides a process for producing the above-mentioned chelate resin, which comprises reacting a resin having nitrile groups with hydroxylamine and/or its derivative and an amino compound other than hydroxylamine and/or its derivative (hereinafter referred to merely as "the amino compound").

- The chelate resin of this invention having in its resin substrate a functional group represented by the formula:



and a functional group represented by the formula:



(II)

1 is characterized in that it has much larger metal ion adsorption ability than the well-known chelate resins having only amidoxime groups.

As the functional group represented by the  
5 formula (II), functional groups in which  $\text{R}_3$  is an amino group, a hydrazino group, an alkylamino group having 1 to 4 carbon atoms, or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms, are preferred. Such a combination that  $\text{R}_1$  and  $\text{R}_2$  are each a  
10 hydrogen atom and  $\text{R}_3$  is a hydrazino group or a polyethylene-polyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms is particularly preferred. The equivalent ratio between the functional groups represented by each of the general formulas (I) and (II), i.e., (II)/(I),  
15 is preferably 0.1 to 1. When the equivalent ratio is less than 0.1, the effect of improving the adsorption ability for metal ions is insufficient. On the other hand, even when the equivalent ratio is increased, the effect of improving the adsorption ability for metal ions does  
20 not increase proportionately thereto, and therefore the equivalent ratio is usually adjusted to 1 or less.

The chelate resin of this invention can be produced by reacting a resin having nitrile groups with hydroxylamine and/or its derivative and the amino  
25 compound.

As the resin having nitrile groups used in

1 the process of this invention, the following polymers,  
copolymers and resins can be usually used:

- (1) Polymers of a vinyl cyanide series monomer or  
copolymers of a vinyl cyanide series monomer and an  
5 ethylenically unsaturated monomer copolymerizable there-  
with. Examples of the vinyl cyanide series monomers are  
acrylonitrile,  $\alpha$ -chloroacrylonitrile, vinylidene  
cyanide, methacrylonitrile, ethacrylonitrile, fumaro-  
dinitrile, crotononitrile, 2-cyanoethyl acrylate, 2-  
10 cyanoethyl methacrylate and the like. Examples of the  
ethylenically unsaturated monomer copolymerizable therewith  
are divinylbenzene, diethylene glycol dimethacrylate,  
ethylene glycol dimethacrylate, polyethylene glycol  
dimethacrylate, vinyl acetate or the like.
- 15 (2) Resins obtained by reacting a polymer having  
an amine-reactive group (hereinafter referred to as  
"the resin having an amine-reactive group") with a nitrile  
compound having one or more amino or imino groups.  
Examples of the amine-reactive group are a chloromethyl  
20 group, a sulfonyl chloride group, a carbonyl chloride  
group, an isocyanate group, an epoxy group, an aldehyde  
group and the like. Examples of the resins having an  
amine-reactive group are a styrene-divinylbenzene  
copolymer, a phenol resin, a polyethylene, a poly-  
25 propylene, a polyvinyl chloride and the like. Examples  
of the nitrile compound having one or more amino groups  
or imino groups are aminoacetonitrile, aminomalononitrile,  
diaminomaleonitrile, dicyandiamide, iminodiacetonitrile,

1 1-amino-2-cyanoethane, 4-aminobenzonitrile, 1-amino-3-cyanopropane and the like. But, the resin having nitrile groups is not limited to those obtained from the above mentioned nitrile compounds.

5           There are particularly preferably used polymers of a vinyl cyanide series monomer such as acrylonitrile, methacrylonitrile, ethacrylonitrile, fumarylonitrile or vinylidene cyanide, or copolymers of any of these vinyl cyanide series monomers and divinylbenzene,  
10 diethylene glycol dimethacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, vinyl acetate or the like.

          The resin having nitrile groups is not particularly limited in its polymerization degree so  
15 long as it is insoluble in water, though in general, those having a polymerization degree of about 500 or more are preferably used.

          As to the form of the resin having nitrile groups, resins in any of powder form, fiber form,  
20 honeycomb form, particle form, spherical form and liquid form may be used, and the form may properly be selected depending on purposes, though in general, spherical or powdery resins are preferably used from the viewpoint of handling.

25           As the hydroxylamine and/or the derivative thereof reacted in order to form amidoxime groups in the resin having nitrile groups which are used in practicing the process of this invention, any one may be used so



1 long as it reacts with the nitrile groups to form  
amidoxime groups represented by the formula (I). As  
such hydroxylamine and/or derivatives thereof, there are  
exemplified hydroxylamine, N-methylhydroxylamine,  
5 N-ethylhydroxylamine, N-aminomethylhydroxylamine, N-  
phenylhydroxylamine, p-(hydroxylamino)phenol, o-acetyl-  
hydroxylamine, and hydrochlorides, sulfates, nitrates,  
phosphates, acetates and the like thereof.

As the amino compound used in order to impart  
10 a group of the formula (II) to the chelate resin in  
practicing the process of this invention, any one may be  
used so long as it reacts with the nitrile groups, has  
such basicity that it can react with acid ions in a  
liquid to form a salt, and forms a complex with a  
15 metal ion. As such an amino compound, there are exempli-  
fied, amines such as ammonia, methylamine, ethylamine,  
propylamine, butylamine and the like; hydrazine and its  
derivatives such as hydrazine, hydrazine hydrate, phenyl-  
hydrazine, p-hydrazinophenol, p-hydrazinobenzoic  
20 acid, p-hydrazinobenzenesulfonic acid, 1-amino-  
piperazine, N-methylhydrazine, 11-oxa-3,4,7,8,14,15-  
hexaazaheptadecane-1,17-diol, acetaldehyde hydrazone,  
hydrazinoethanol, isothiosemicarbazide, thiocarbono-  
hydrazide, semicarbazide and the like; azanes, azenes  
25 and derivatives thereof, such as triazane, triazene,  
tetrazane, tetrazene, tetrazadiene, pentazane, 1-  
methyltriazane, 1-methyl-3-propyltriazane, 3-methyl-  
triazene, 3-methyl-1-tetrazene, ethyltetrazanoacetate

- 1 and the like; amidine and its derivatives such as  
acetamidine, hexaneamidine, cyclohexanecarboxy-  
amidine, p-amidino-1-benzoic acid and the like;  
guanidine and its derivatives such as guanidine,  
5 biguanide, 1,3-dimethylguanidine, 1,1,2-trimethyl-  
guanidine and the like; amidoxime and its derivatives  
such as formamidoxime, acetamidoxime, imidazole-2-  
carboxamide-o-ethyloxime, N-methylacetamidoxime  
and the like; amidrazone and its derivatives  
10 such as benzamide hydrazone, benzamido hydrazido  
imide, hydrazine, 2-thenohydrazide hydrazone,  
N<sup>2</sup>,N<sup>4</sup>-dimethyl-4-thiazolecarbohydrazide hydrazone,  
benzaldehyde hydrazone and the like; formazan and its  
derivatives such as formazan, 3-phenyl formazan,  
15 1,3-diphenylformazan, 1,3-dimethylformazan and the  
like; and polyethylenepolyamines and their derivatives  
such as ethylenediamine, diethylenetriamine, triethylene-  
tetramine, tetraethylenepentamine, pentaethylenehexamine,  
hexamethylenediamine, trimethylenediamine, tetramethylene-  
20 diamine, pentaethylenediamine and the like.

The reaction of the resin having nitrile groups  
with the hydroxylamine and/or its derivative and the  
amino compound is usually effected by a method wherein  
the resin having nitrile groups is reacted with hydroxyl-  
25 amine and/or its derivative and the amino compound which  
coexist with each other, to form functional groups of  
each of the formulas (I) and (II) at the same time.  
Said reaction can also be effected by a method comprising

1 previously reacting the resin having nitrile groups with  
hydroxylamine or its derivative, then adding the amino com-  
pound, and further allowing the resulting mixture to reac-  
tion, or by a method comprising previously reacting the  
5 resin having nitrile groups with the amino compound, and  
then reacting the reaction product with hydroxylamine  
and/or its derivative.

The reaction of the resin having nitrile groups  
with hydroxylamine and/or its derivative and the amino  
10 compound can be effected at ordinary temperatures (about  
20°C) to 150°C, preferably at 50° to 120°C in the  
absence of a solvent or in the presence of a solvent.  
Examples of the solvent are water, methanol, ethanol,  
propanol, butanol, N,N-dimethylformamide, formamide,  
15 N,N-dimethyl sulfoxide, toluene, xylene, carbon  
tetrachloride, 1,2-dichloroethane and the like. When  
the reaction temperature is lower than ordinary tempera-  
tures, the reaction rate decreases, so that the reaction  
must be effected for a long time, and when the reaction  
20 temperature is higher than about 150°C, a phenomenon  
of the decomposition of the formed functional groups  
occurs. Therefore, such reaction temperatures are not  
preferable.

The reaction is effected at the temperature  
25 described above, usually for about 0.1 to 24 hours,  
preferably for 0.5 to 6 hours. But a still longer  
reaction time may be used. Although the reaction is usual-  
ly effected at atmospheric pressure, it may be effected

1 under pressure.

As to the reaction proportions of the hydroxyl-  
amine and/or the derivative thereof and of the amino  
compound to the resin having nitrile groups, it is  
5 sufficient that the hydroxylamine and/or the derivative  
thereof and the amino compound are used in amounts of  
1/5 mole or more and 1/20 mole or more, respectively, per  
equivalent of the nitrile groups in the resin. However,  
since the employment of the reactants in larger amounts  
10 than are necessary is accompanied by recovery treatment  
after the reaction and hence makes the treatment  
procedure troublesome, the hydroxylamine and/or the  
derivative thereof and the amino compound are preferably  
used in amounts in the ranges from 2/5 to 10 moles and  
15 from 1/10 to 3 moles, respectively, per equivalent of  
the nitrile groups in the resin. When the reaction pro-  
portions of the hydroxylamine and/or the derivative thereof  
and of the amino compound to the resin having nitrile  
groups are smaller than those described above, the amounts  
20 of chelate-forming functional groups introduced decreases,  
so that the metal adsorption capacity of the resulting  
reaction product chelate resin decreases. Therefore,  
it is not desirable.

When the hydroxylamine and/or the derivative  
25 thereof used in the above-mentioned reaction is a salt  
with hydrochloric acid, sulfuric acid, nitric acid,  
phosphoric acid, acetic acid or the like, it is  
sufficient that the resin having nitrile groups is

1 reacted with the hydroxylamine derivative and the amino  
compound in the presence, in the reaction system, of the  
same amount as said salt or more of sodium hydroxide,  
potassium hydroxide, a tertiary amine such as trimethyl-  
5 amine, triethylamine, pyridine, N,N-dimethylaniline or  
the like, or the aforesaid amino compound.

The reaction product produced in the manner  
described above may be used as a chelate resin as it is  
or after being washed and then dried.

10 The chelate resin produced by the process of  
this invention contains groups of each of the formula (I)  
and the formula (II) as main functional groups, and  
although the reason why the chelate resin produced by the  
process of this invention has a higher adsorption rate  
15 and a larger adsorption capacity than those of the  
heretofore well-known amidoxime type chelate resins  
is not apparent, it is presumed to be as follows.

That is to say, the reason is thought to  
be that in the reaction of the resin having nitrile  
20 groups with the hydroxylamine and/or the derivative  
thereof and the amino compound, owing to the electrical  
interaction between the amino compound and the nitrile  
groups in the resin, the reactivity of the hydroxylamine  
and/or the derivative thereof with the nitrile groups  
25 is improved as compared with that in a system free from  
the amino compound, resulting in an increase of the amount  
introduced of the functional group represented by the  
formula (I), and that owing to the interaction between

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1 the functional group represented by the formula (II),  
which is formed by the reaction of the nitrile groups with  
the amino compound, and the functional group represented  
by the formula (I), the chelate adsorption ability  
5 is increased as compared with that in the case where the  
functional group of the formula (I) alone is present.

The chelate resin produced by the process of  
this invention can very effectively be utilized for the  
adsorption and removal of metal ions such as uranium,  
10 gallium, indium, copper, iron, mercury, lead and the  
like.

According to the process of this invention  
described above in detail, there is such an advantage in  
that there can be produced a chelate resin having a  
15 high adsorption rate and large adsorption capacity  
as compared with the well-known amidoxime type chelate  
resins. Accordingly, when the chelate resin obtained by  
the process of this invention is used, the superficial  
velocity in column can be increased owing to the high  
20 adsorption rate and the large adsorption capacity:  
therefore said chelate resin is very effective for  
treating a large amount of a liquid, has advantages of,  
for example, low construction and operation costs of the  
treating facilities, and hence has a very high industrial  
25 value.

This invention is further explained below in  
more detail referring to Examples, wherein all parts and  
percents are by weight unless otherwise specified.

1 Example 1

To 61 parts of a resin having nitrile groups, i.e. an acrylonitrile-divinylbenzene copolymer having a degree of crosslinking of 10 mole% and a particle size of 20 to 50 mesh were added 139 parts of hydroxylamine hydrochloride, 100 parts of hydrazine hydrate and 300 parts of water. The resulting mixture was reacted at 90° to 107°C for 4 hours, followed by filtration and washing, to obtain 169 parts by weight (undried) of a chelate resin. In the chelate resin obtained, there were detected a functional group  $\begin{array}{c} -C = NOH \\ | \\ NH_2 \end{array}$  in an amount of 6.0 mole/liter resin and a functional group  $\begin{array}{c} -C = NH \\ | \\ NHNH_2 \end{array}$  in an amount of 1.8 mole/liter resin. To 50 ml of an aqueous sodium aluminate solution containing 197 ppm of Ga obtained from the production process of alumina by the Bayer process was added 7 ml of the chelate resin obtained, and the resulting mixture was shaken for 20 hours and then separated into the chelate resin and an aqueous layer. The concentration of Ga remaining in the aqueous layer was measured to be 14 ppm. To 50 ml of enriched sea water containing 110 ppm of U was added 1 ml of the chelate resin obtained, and the resulting mixture was shaken for 20 hours and then separated into the chelate resin and an aqueous layer. The concentration of U remaining in the aqueous layer was measured to be 17 ppm.

1 Examples 2 to 13

A reaction was effected in the same manner as in Example 1, except that the hydrazine hydrate, i.e., the amino compound used in Example 1 and the used amount thereof were replaced by the individual amino compounds and amounts shown in Table 1, to synthesize a chelate resin. The thus obtained chelate resins were subjected to performance characteristic tests. The results are shown in Table 1.




Table 1

Exam- ple	Amino compound		Chelate resin			Adsorption ability test	
	Kind	Amount	Yield (dried)	Functional group (I) mole/liter resin	Functional group (II) mole/liter resin	Ga (ppm)	U (ppm)
2	p-Hydrazino- phenol	parts 186	parts 153	$\begin{array}{c} \text{-C=NOH} \\   \\ \text{NH}_2 \end{array}$	$\begin{array}{c} \text{-C=NH} \\   \\ \text{NHNH} \langle \text{C}_6\text{H}_4 \rangle \text{OH} \end{array}$	27	21
3	2-Hydrazino- ethanol	114	167	"	$\begin{array}{c} \text{-C=NH} \\   \\ \text{NHNHCH}_2\text{CH}_2\text{OH} \end{array}$	19	21
4	Guanidine	89	154	"	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNC (=NH) -NH}_2 \end{array}$	12	14
5	1,1,2-Tri- methylguanidine	152	183	"	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HN-C (=N-CH}_3\text{)N(CH}_3\text{)}_2 \end{array}$	13	14

- Cont'd -

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Table 1 (cont'd)

6	Formamidoxime	90	147	$\begin{array}{c} \text{-C=NOH} \\   \\ \text{NH}_2 \end{array}$	4.9	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNCH=NOH} \end{array}$	1.5	23	20
7	Formhydrazide	81	147	"	4.9	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNNHCOH} \end{array}$	1.5	24	21
8	Formamidine	66	153	"	5.0	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNCH=NH} \end{array}$	1.5	21	19
9	Benzaldehyde hydrazone	180	143	"	4.7	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNN=NCH-} \end{array}$ 	1.2	28	23
10	Ethylenediamine	90	156	"	5.8	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNCH}_2\text{CH}_2\text{NH}_2 \end{array}$	1.7	15	15
11	Diethylenetri- amine	155	184	"	5.9	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_2 \end{array}$ H	1.7	13	14

- Cont'd -

Table 1 (Cont'd)

12	Triethylene- tetramine	219	189	$\begin{array}{c} \text{-C=NOH} \\   \\ \text{NH}_2 \end{array}$	5.9	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_3\text{H} \end{array}$	1.6	13	14
13	Semicarbazide	144	153	"	4.8	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HNNHCONH}_2 \end{array}$	1.4	25	22

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1 Example 14

To 82 parts of a resin having nitrile groups, i.e., vinylidene cyanide-divinylbenzene having a degree of crosslinking of 8 mole% and a particle size of 20 to 50 mesh were added 164 parts of hydroxylamine sulfate, 267 parts of a 30% aqueous sodium hydroxide solution and 103 parts of diethylene-triamine. The resulting mixture was reacted at 90° to 103°C for 2 hours, followed by filtration and washing, to obtain 284 parts (undried) of a chelate resin. In the chelate resin obtained, there were detected a functional group  $\text{-C} = \text{NOH}$  in an amount of 9.8 mole/liter

$$\begin{array}{c} | \\ \text{NHNH}_2 \end{array}$$

resin, and a functional group  $\text{-C} = \text{NH}$  in an amount

$$\begin{array}{c} | \\ \text{NH}(\text{CH}_2\text{CH}_2\text{NH})_2\text{H} \end{array}$$

of 3.0 mole/liter resin. Performance characteristic tests on the resin obtained were carried out by the same methods as in Example 1 to find that the Ga concentration in the aqueous layer was 3 ppm and the U concentration therein 5 ppm.

Examples 15 to 18

20 A reaction was effected in the same manner as in Example 14, except that the kind and amount of the resin having nitrile groups were replaced by the individual resins and amounts shown in Table 2, to synthesize a chelate resin. The thus obtained chelate resins were subjected to performance characteristic tests. The results are shown in Table 2.

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Table 2

Exam- ple	Resin having nitrile group		Chelate resin				Adsorption ability test	
	Kind	Amount	Yield (un- dried)	Functional group (I) mole/liter resin	Functional group (II) mole/liter resin	Ga (ppm)	U (ppm)	
15	Methacrylonitrile- divinylbenzene copolymer having a degree of cross- linking of 6 mole% and a particle size of 20 to 50 mesh	parts 75	parts 220	-C=NOH   NH <sub>2</sub>	-C=NH   HN(CH <sub>2</sub> CH <sub>2</sub> NH) <sub>2</sub> H	11	12	
16	Acrylonitrile- diethylene glycol dimethacrylate copolymer having a degree of crosslinking of 20 mole% and a particle size of 20 to 50 mesh	86	243	"	"	16	17	

- Cont'd -

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Table 2 (Cont'd)

17	Acrylonitrile-ethylene glycol dimethacrylate copolymer having a degree of crosslinking of 25 mole% and a particle size of 20 to 50 mesh	83	237	$\begin{array}{c} \text{-C=NOH} \\   \\ \text{NH}_2 \end{array}$	4.8	$\begin{array}{c} \text{-C=NH} \\   \\ \text{HN(CH}_2\text{CH}_2\text{NH)}_2\text{H} \end{array}$	1.7	22	23
18	Polyacrylonitrile fiber	53	147	"	6.4	"	2.2	10	12

1 Example 19

To 67 parts of a resin having nitrile groups,  
i.e., an acrylonitrile-divinylbenzene copolymer having a  
degree of crosslinking of 10 mole% and a particle  
5 size of 20 to 50 mesh were added 94 parts of N-methyl-  
hydroxylamine, 50 parts of hydrazine hydrate and 400 parts  
of water. The resulting mixture was reacted at 70 to  
103°C for 6 hours, followed by filtration and washing  
to obtain 224 parts (undried) of a chelate resin. In the  
10 chelate resin obtained, there were detected a functional  
group  $\begin{array}{c} -C = NOH \\ | \\ HNCH_3 \end{array}$  in an amount of 5.3 mole/liter resin, and  
a functional group  $\begin{array}{c} -C = NH \\ | \\ HNNH_2 \end{array}$  in an amount of 2.3 mole/liter  
resin. Performance characteristic tests on the resin  
obtained were carried out by the same methods as in  
15 Example 1 to find that the Ga concentration in the  
aqueous layer was 18 ppm and the U concentration therein  
23 ppm.

Examples 20 to 23

A reaction was effected in the same manner as  
20 in Example 19, except that the kinds and amounts of the  
hydroxylamine derivative and the amino compound used in  
Example 19 were changed as shown in Table 3, to synthesize  
a chelate resin. The thus obtained chelate resins were  
subjected to performance characteristic tests. The results  
25 are shown in Table 3.

Table 3

Exam- ple	Hydroxylamine derivative		Amino compound		Chelate resin			Adsorption ability test	
	Kind	Amount	Kind	Amount	Yield (dried)	Functional group (I) mole/ liter resin	Functional group (II) mole/ liter resin	Ga (ppm)	U (ppm)
20	N-Ethyl- hydroxyl- amine	183 parts	Hydrazine	32 parts	270	-C=NOH   HNC <sub>2</sub> H <sub>5</sub>	-C=NH   NHNH <sub>2</sub>	21	26
21	Hydroxyl- amine hydro- chloride	69	Acetamidine	116	207	-C=NOH   NH <sub>2</sub>	-C=NH   HN-C(=NH)CH <sub>3</sub>	16	19
22	N-amino- methyl- hydroxylamine	126	Semi- carbazine	75	243	-C=NOH   HNC <sub>2</sub> H <sub>2</sub> NH <sub>2</sub>	-C=NH   HNNHCONH <sub>2</sub>	18	21
23	Hydroxyl- amine	99	1-Amino- piperazine	87	222	-C=NOH   NH <sub>2</sub>	-C=NH   HN-N <sub>2</sub>   NH	18	23



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1 Comparative Example 1

A reaction was effected in the same manner as in Example 1, except that the hydrazine hydrate used in Example 1 was replaced by 80 parts of sodium hydroxide, 5 to synthesize a chelate resin. As a result, 147 parts (undried) of the chelate resin was obtained. In the chelate resin obtained, there was detected a functional group  $\begin{array}{c} \text{-C = NOH} \\ | \\ \text{NH}_2 \end{array}$  in an amount of 2.2 mole/liter resin.

Performance characteristic tests on the chelate 10 resin obtained were carried out by the same methods as in Example 1 to find that the concentration of Ga remaining in the aqueous layer was 89 ppm and the U concentration 34 ppm.

Comparative Example 2

15 A reaction was effected in the same manner as in Example 14, except that 86 parts of an acrylonitrile-diethylene glycol dimethacrylate polymer having a degree of crosslinking of 20 mole% and a particle size of 20 to 50 mesh was used as a resin having nitrile groups and 20 that 103 parts of the diethylenetriamine was omitted, to synthesize a chelate resin. As a result, 211 parts (undried) of the chelate resin was obtained. The chelate resin obtained contained a functional group  $\begin{array}{c} \text{-C = NOH} \\ | \\ \text{NH}_2 \end{array}$  in an amount of 1.9 mole/liter resin. Performance 25 characteristic tests on the chelate resin obtained

1 were carried out by the same methods as in Example 1  
to find that the concentration of Ga remaining in the  
aqueous layer was 93 ppm and the U concentration 32 ppm.

### Comparative Example 3

5                   Adsorption capacity tests on Duolite CS-346  
(manufactured by Diamond Shamrock Corp.), a commercially  
available chelate resin having amidoxime groups were  
carried out by the same methods as in Example 1 to find  
that the concentration of Ga remaining in the aqueous  
10 layer was 114 ppm and the U concentration 37 ppm.

From Examples 1 to 23 and Comparative Examples  
1 to 3, it is clear that the chelate resins obtained by  
effecting the reaction of a resin having nitrile groups  
with hydroxylamine and/or its derivative according to the  
15 process of this invention in the presence of an amino  
compound have a higher adsorption rate and a larger  
adsorption capacity for metal ions than those of amidoxime  
group type chelate resins produced by a well-known  
process. Thus, the present invention is industrially very  
20 useful.

WHAT IS CLAIMED IS:

1. A chelate resin having a functional group represented by the formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are each independently a hydrogen atom, an alkyl group, an aminoalkyl group, a phenyl group or a substituted group thereof and a functional group represented by the formula:



wherein  $\text{R}_3$  is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group or a substituted group thereof.

2. A chelate resin according to Claim 1, wherein in the functional group represented by the formula (II),  $\text{R}_3$  is an amino group, a hydrazino group, an alkylamino group having 1 to 4 carbon atoms, or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms.

3. A chelate resin according to Claim 1, wherein in the functional group represented by the formula (I),  $\text{R}_1$  and  $\text{R}_2$  are independently a hydrogen atom, and in the functional group represented by the formula (II),  $\text{R}_3$  is

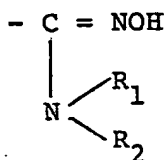
a hydrazino group or a polyethylenepolyamino group having 2 to 10 carbon atoms and 2 to 6 nitrogen atoms.

4. A chelate resin according to Claim 1, wherein the equivalent ratio of the functional group of the formula (II) to that of (I), (II)/(I), is 0.1 to 1.

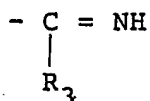
5. A process for producing a chelate resin of Claim 1, which comprises reacting a resin having nitrile groups with hydroxylamine and/or a derivative thereof and an amino compound other than the hydroxylamine and derivatives thereof.

6. A process according to Claim 5, wherein the proportions of the hydroxylamine and/or the derivative thereof and the amino compound to the resin having nitrile groups used are 1/5 mole or more of hydroxylamine and/or the derivative thereof and 1/20 mole or more of the amino compound per equivalent of the nitrile groups.

7. A chelate resin having a functional group of the formula:



wherein  $R_1$  and  $R_2$  are each independently a hydrogen atom, an alkyl group, an aminoalkyl group, a phenyl group or a substituted group thereof and a functional group of the formula:



wherein  $\text{R}_3$  is an amino group, an alkylamino group, a polyethylenepolyamino group, a hydrazo group, a hydrazino group, a hydrazono group, an amidino group, a guanidino group, a semicarbazide group or a substituted group thereof, obtainable by reacting a resin having nitrile groups with hydroxylamine and/or a derivative thereof and an amino compound other than the hydroxylamine and derivatives thereof.

8. A chelate resin according to Claim 7, wherein the resin having nitrile groups is at least one member selected from the group consisting of homopolymers of acrylonitrile, methacrylonitrile, ethacrylonitrile, fumarylonitrile, and vinylidene cyanide and copolymers of a monomer selected from the group consisting of acrylonitrile, methacrylonitrile, ethacrylonitrile, fumarylonitrile and vinylidene cyanide, and a monomer selected from the group consisting of divinylbenzene, diethylene glycol dimethacrylate, ethylene glycol dimethacrylate, polyethylene glycol dimethacrylate and vinyl acetate.

9. A chelate resin according to Claim 7, wherein the resin having nitrile groups has a degree of polymerization of 500 or more.

10. A process according to Claim 5, wherein the reaction is carried out at a temperature of 20 to 150°C.

11. The use of the resins according to any one of claims 1 to 10 for removing metal ions from liquids containing metal ions.